(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 342 276
A1

EUROPEAN PATENT APPLICATION

(21) Application number: 88200973.1

(51) Int. Cl.4: C08F 8 44 . C09D 5 14

(22) Date of filing: 16.05.88

(43) Date of publication of application:
23.11.89 Bulletin 89 47

(84) Designated Contracting States:
DE FR GB NL

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(54) Preparation of metal containing resin composition and antifouling paint containing said resin composition.

(57) A resin composition to be used as a resinous vehicle for an antifouling paint. An object is attained by a method comprising reacting a mixture of

A a polymer containing base resin

B a metallic salt of low boiling organic basic acid in which the metal is bivalent metal and the acid has 2 or more valence and lesser dissociation constant than those of the metallic salt and

C an organic monobasic acid

to give a resin composition. An antifouling paint which ...

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Preparation of metal containing resin composition and antifouling paint containing said composition

Field of invention

The present invention relates to a preparation of metal containing resin composition which is characterized by having metal ester bonding at the end portion of pendant chain. The invention also concerns an antifouling paint containing as resinous vehicle the thus formed metal containing resin composition.

Backgroud of the invention

Today, it is very common to apply onto ship's bottom and the like an antifouling coating composition comprising an organic or inorganic antifouling agent and a resinous binder as vinyl resin, alkyd resin and the like.

In that case, since the antifouling effect is fully dependent on the antifouling agent dissolved out of the coating and the dissolution of said agent is primarily a diffusion phenomenon caused by a concentration gradient of said agent in the coating, it is unable to expect a long lasting, stable antifouling effect with them.

Furthermore, since the water insoluble resinous component will, after dissolution of said agent from the coating, form a skeleton structure, there are additional problems as increase in resistance of friction between the ship surface and water, lowering of sailing speed, increase in sailing fuel and the like. Under the circumstances, an antifouling coatiang composition comprising an antifouling agent and a hydrolyzable resin vehicle capable of forming a comparatively tough coating and being gradually decomposed by hydrolysis in sea water has become the center of public attention.

The present inventors had already found that a class of polyester resins having a number of metal-ester bondings in their polyester backbone chains are useful as a resinous vehicle in a polishing type antifouling paint, and applied for patent as Japanese Patent Application Nos. 165922/81 and 196900/83.

Such resins are of the nature of being easily hydrolyzed, under weak alkaline condition as in sea water, at the metal-ester bonding portions, disintegrated to a number of small, low molecular weight segments and dissolved in sea water. However, said resins are primarily of comparatively low molecular weight (e.g. up-to about 3000) and are poor in film-forming property, and therefore, said coating compositions still have the problems of easy occurrence of cracks and peeling of the formed coatings.

If the molecular weight of said polyester resin is increased to a moderate level, it is indeed possible to improve the film-forming property, but, at that time, it will necessarily be attended with a marked decrease in hydrolysis property of the resin. To compensate the same, if the metal-ester bonding in the backbone chain of the resin is increased in number, there will give additional problems that the resulted resin is only soluble in a polar solvent and not in most solvents commonly used in a coating composition, and that the formed coating is swollen with sea water. These attemps would therefore, give no fruitful results, and thus, there leaves much to be desired.

An attempt has also been made to use a resin whose side chain has a trialkyl tin ester portion as a terminal group. In this type of resin, polarity of the resin is gradually increased in proportion to the progress in hydrolysis of said ester portion, and the resin is finally dissolved in sea water.

Typical examples of such resins are acrylic resins having as a constitutional element tri organo tin salts of α, β-unsaturated basic acids. In this case, in order to obtain a stabilized, tough coating, the resin should preferably be free from hydrophilic groups if circumstances allow, and in order to ensure the dissolution of the hydrolyzed resin in sea water, the resin should preferably have as many hydrophilic groups as possible, i.e. more than a certain critical range, after said hydrolysis.

Therefore, in the preparation of such resin by the copolymerization of tri organo tin salt of α, β-unsaturated basic acid and other acrylic vinyl monomers, attempts have been made such that the former is presented in a higher concentration in the reaction system and the latter is selected from the members with no or least amount of hydrophilic groups. Thus, a copolymer of acrylate, acrylamide, styrene and the like containing 55 to 70 wt% of tri organo tin salt of α, β-unsaturated monobasic acid has been prepared and practically used.

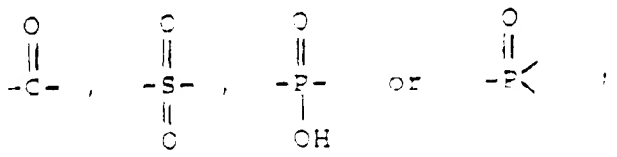
In this type of resin, differing from the aforesaid polyester resin having metal-ester bondings in its main chain, hydrophilic carboxyl groups are generated at the time when the tri organo tin portions at the side chains are released through hydrolysis and the resin is only dissolved in sea water at the stage where the

composition of said carboxyl group-containing polymer. This method is highly advantageous and excellent. However, there remains a problem that a considerable quantity of highly abrasive and hard inorganic compound are essential. Therefore, from point hygienic and economic point of view, it has been urged for cutting the amount of or replacing the use of such material.

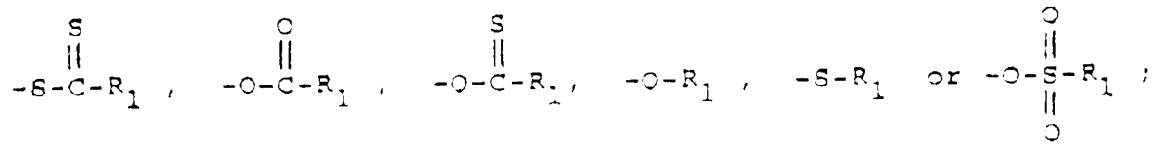
Under the circumstances, the inventors have offered previously (Japanese Patent Application No. 108434/85), as a hydrolyzable resin composition which has an excellent self-forming property, and which resin is characterized by having at the side chain portions a carboxyl group capable of resulting a hydrophilic group through hydrolysis, being hydrolyzed and dissolved in sea water at an appropriate rate and being prepared without the necessity of using a inorganic fine compound which is expensive and toxic material, a composition consisting essentially of a resin having at least one side chain bearing at least one terminal group of the formula:

$-X\{O-M-R\}_x$

where in X represents



M is a metal selected from zinc, copper and tributyltin;
x is an integer of 1 to 2; R represents an organic acid residue selected from



and R_1 is a monovalent organic residue.

The said resin composition has been prepared by either one of the following methods:

(1) A mixture of (a) a metal oxide, hydroxide, sulfide or chloride, (b) a monovalent organic acid or its alkali metal salt and (c) a polymerizable unsaturated organic acid or its alkali metal salt is reacted under stirring at a temperature lower than the decomposition temperature of the polymerizable unsaturated organic acid and the by-product substances as alkali metal chloride, water, monovalent organic acid metal ester, a functional polymerizable unsaturated organic acid metal salt and the like are removed to obtain a purified metal ester between the polymerizable unsaturated organic acid and the monovalent organic acid.

Thus obtained metal ester between the polymerizable unsaturated organic acid and the monovalent organic acid or the mixture of said metal ester and the monovalent organic metal ester is then subjected to a homopolymerization or a copolymerization with other copolymerizable monomer to give the desired resin having at least one side chain bearing at least one metal ester containing terminal group.

(2) A mixture of (a) a resin having a side chain of organic acid or its alkali metal salt, a monovalent organic acid or its alkali metal salt and (b) a metal compound selected from metal oxide, metal hydroxide, metal sulfide or metal chloride is heated under stirring at a temperature lower than the decomposition temperature of the polymerizable unsaturated organic acid and the by-product substances are removed to obtain a resin having at least one side chain bearing the desired metal ester terminal group.

(3) Alternatively, the desired product may be prepared by reacting a resin having at least one side chain bearing an organic acid or its alkali metal salt and a metal ester of the monovalent organic acid.

The amount of the [illegible] is preferably [illegible] the amount of the [illegible] is more than the molar equivalent of the [illegible] is used.

[illegible]

In the second method, since the reaction involved is a neutralization reaction, there is a considerable difficulty in the control of reaction speed and in the extreme case, there occurs gelation of the reaction product.

And, in this third method, since the reaction involved is a kind of equilibrium reaction and no particular regard is payed to removed by-produced monobasic acid out of the reaction system, such acid always remain in the product in the form of free acid and causes blisters in the coating exposed to ionic atmosphere. Furthermore, such acid may be reacted with an antifouling agent in a coating composition under preparation and storage conditions, causing a remarkable decrease in quality of the coating composition or the coating prepared therefrom. Free acid may also cause corrosion of base plate.

It is, therefore, an object of the invention to provide a novel method for the preparation of a metal containing resin composition which is totally free from the abovesaid problems. An additional object of the invention is to provide a method in which a variety of metals may be freely used and such metal can be incorporated in a resin in various forms bonded with carboxylic acid, sulfonic acid and phosphoric acid.

A further object of the invention is to provide a method by which a high boiling organic basic acid can be introduced in side chains of a resin in metal ester form and in a higher reaction yield.

Yet another object of the invention is to provide an antifouling paint which is excellent in film-forming property, and capable of resulting a coating with no blister and being excellent in polishing and antifouling effects.

Summary of the invention

According to the invention, the aforesaid objects can be attained with a process for preparing metal containing resin composition comprising reacting a mixture of (A) acid group containing base resin, (B) metallic salt of low boiling organic basic acid in which the metal is selected from the members having 2 or more valence and lesser ionization tendency than those of alkali metals, and (C) high boiling organic monobasic acid at an elevated temperatrue while removing the formed low boiling organic basic acid out of the system, and an antifouling paint containing as resinous vehicle and aforesaid resin composition.

Preferred embodiments of the invention

In the present invention, a base resin having acid groups as caboxylic acid, sulfonic acid or phosphoric acid residue is reacted with a metallic salt of low boiling organic basic acid and a high boiling organic monobasic acid at an elevated temperature and the by-produced (through ester exchange reaction) low boiling organic basic acid is removed out of the system through, for example, thermal decomposition, vacuum distillation, azeotropic distillation with water or organic solvent and the like.

The reactions involved are all equilibrium reactions and they are, differing from a vigorous neutralization reaction, easily controlled. Furthermore, there is no fear of remaining a quantity of undesired low boiling basic acid in the reaction product and there is no problem of requiring a larger quantity of initiator.

Therefore, the present method is very useful for the preparation of hydrolysis type, metal containing resin composition for coating use.

Additional benefit resides in the point that high boiling organic acid can be easily and advantageously introduced in a base resin through metal ester bonding, which is hardly possible by the conventional ester exchange reaction between an acid group containing base resin and metallic ester of organic monobasic acid.

The base resin used in the present invention may be any of the know, coating-use resin having acid groups at the side chains thereof. Examples are vinyl resin, polyester resin, alkyd resin, epoxy resin and the like.

The metallic salts of low boiling basic acids are metallic salts of organic carboxylic acids, organic sulfonic acids or organic phosphoric acids each having a boiling point of 100° to 240°C. Said metallic component may be any metals having 2 or more valence and lesser ionization tendency than those of alkali metals.

Examples are the members belonging to Ib (e.g. Cu, Ag) IIa (e.g. Ca, Ba), IIb (e.g. Zn, Cd, Hg), IIIa (e.g. Sc, Y), IIIb (e.g. Al, In), IVa (e.g. Ti, Zr), IVb (e.g. Sn, Pb, Si), Va (e.g. V, Nb), VIa (e.g. Cr, Mo, W), VIb (e.g. Se, Te), VIIa (e.g. Mn) and VIII (e.g. Fe, Co, Ni) groups of Periodic Table.

Though the metallic salts may likewise be organic metal salts as dibutyltin acetate, dibutyltin sulfate and the like, they must be of polyorganometal salt type.

In this invention, the term "low boiling" is used in contrast to the term "high boiling" and more is not particular limitation of the boiling range of the respective organic basic acid. However, in practice the low boiling organic basic acid should preferably have a boiling point of 100° to 230°C.

In general, a metallic salt is liable to be decomposed by heating. Therefore, the reaction temperature must be settled in a range which is lower than the decomposition temperature of the metallic salt used.

For this reason, the low boiling organic basic acid should preferably be easily removed out of the system at a temperature which is lower than the decomposition temperature of the metallic salt and preferably 150°C or more, by either method of thermal decomposition, vacuum distillation, azeotropic distillation with water or azeotropic distillation with an organic solvent.

Particularly preferable low boiling organic acids are acetic acid, propionic acid, oxalic acid, lactic acid, pivalic acid, valeric acid, dimethyl acetic acid, enanthic acid, cyclohexane carboxylic acid, chloroacetic acid, glycolic acid, acrylic acid, methacrylic acid and the like. Their corresponding sulfonic acids and phosphonic acids may likewise be used advantageously.

The metallic salts of low boiling organic basic acids may easily be prepared by the azeotropic reaction of metal hydroxide or oxide and an organic basic acid or the equimolar reaction of metallic sulfonate, nitrate or halide and an alkali metal salt of organic basic acid.

Various metallic salts of low boiling organic basic acids are available in the market, too.

As the high boiling organic monobasic acid, it should preferably have a far higher boiling point, at least 20°C higher boiling point, than that of the low boiling organic acid. More preferably, it should have a bioactivity, as fungicidal, antifouling and other similar activities. They may be any organic acids including aliphatic, aromatic, alicyclic and heterocyclic organic acids.

Typical examples are benzoic acid, salicylic acid, 3,5-dichlorobenzoic acid, lauric acid, stearic acid, nitrobenzoic acid, indoleic acid, naphthenic acid, 12-hydroxy stearic acid, fluoroacetic acid, oxiric acid, abietic acid, mercaptobenzomiazole, O-cresotinic acid, naphthol-1-caboxylic acid, p-phenyl benzene sulfonic acid, p-oxy-benzoic acid, chloroacetic acid, dichloroacetic acid, naphthenic acid, 3-naphthalene sulfonic acid, naphthol-1-sulfonic acid, 5-chloro-, x-bis (3,5-dichloro-2-hydroxy phenyl) toluene sulfonic acid, p-phenyl benzoic acid, p-toluene sulfonic acid, p-benzene chlorosulfonic acid, dimethyl dithic carbamic acid, diethyl dithic carbamic acid, dibutyl dithic carbamic acid, ethocholic acid, phenoxy acetic acid, 2,4-dichlorophenoxy acetic acid, oleic acid, versatic acid, nicotinic acid, penicillic acid and the like. The reaction may be easily proceeded by merely mixing the materials and heating the mixture. At that time, it is however, necessary to continuously remove the formed low boiling organic basic acid out of the system by, for example, thermal decomposition, vacuum distillation, azeotropic distillation with water or an organic solvent and the like.

The inventors have also found that the reaction time could be markedly shorten when the reaction is carried out in the presence of 0.01 to 5% by weight, preferably 0.03 to 2% by weight of the resinous acid of an organic tin catalyst or an acid catalyst.

Thus obtained resin composition is stable and free from a potentiale amount of low boiling organic basic acid which will cause blisters in the formed film or coating. Since an amount of metal ester bondings are included, thus formed film or coating can be hydrolyzed under sea-water.

Therefore, the present resin composition may be used in various fields including paint, medicine and agricultural chemical industries, as hydrolyzable film-forming resins. Among them, particular preference is given to resinous vehicle in an antifouling paint.

Thus, in the second aspect of the invention, it provides an antifouling paint containing as resinous vehicle a metal containing resin composition obtained by the method of this invention.

In this particular application, since a hydrolysis rate of the resulting coating is low, unless the acid group containing base resin should preferably have an acid value of 25 to 350 mg KOH/g. This is because, if the acid value is less than 25 mg KOH/g, the desired hydrolysis rate of the coating may not be further attained due to bulky metal ester bondings, whereas if the acid value is more than 350 mg KOH/g, there are sometimes arising various disadvantages.

As to the molecular weight of the present resin containing base resin, it is not particularly limited, but in general, it is preferable to be in the range of 1,000 to 100,000, more preferably 2,000 to 50,000. If the molecular weight is less than 1,000, the coating film tends to be brittle, whereas if more than 100,000, the viscosity of the resin solution becomes too high to be difficult to handle.

The present antifouling paint is characterized by containing as resinous vehicle the abovementioned metal containing resin composition, and however, this paint may further contain, as option ingredients, the following.

(1) Antifouling agent:

Various known antifouling agents including antifouling agents for ship bottom paint, bactericides, fungicides, agricultural chemicals or the like may be satisfactorily used. However, when the solubility of such compound in sea water is less than 0.01 ppm, it is unable to get a good balance between the dissolution speed of the coating and dissolving power of the antifouling agent, and therefore, no effective antifouling can be expected with said compound. On the other hand, when the solubility of such compound in sea water is over 5000 ppm, the formed coating will absorb water and the contained antifouling agent will selectively dissolve out and hence, it is unable to get a desired antifouling efficiency.

Therefore, the solubility of antifouling agent in sea water should preferably be in a range of 0.01 to 5000 ppm, and more preferably 0.1 to 50 ppm.

Examples of such antifouling agents are powder or flake form of copper, zinc, manganese or the like; oxides, suboxides, rhodanides, carbamates, hydroxides or pyrithiones of copper, zinc, manganese and the like; benzothiazole compounds; phthalimide compounds; sulfamide compounds; sulfide compounds; quinoline compounds; phthalonitrile compounds; carbamate compounds; isothiazoline compounds; triphenyl tin compounds; carbamic acid compounds and esters; thiocyanate compounds and the like.

More specifically, they must be classified in the following groups from the sustained-release point of view.

(A) most preferable members:

copper powder, copper suboxide, copper rhodanide, zinc bis (dimethyl dithiocarbamate), zinc ethylene bis (dithiocarbamate), manganese ethylene bis (dithiocarbamate), copper bis (dimethyl dithiocarbamate), 2-thiocyanomethylthio benzothiazole, tetramethyl thiuram disulfide, 8-hydroxy quinoline, zinc pyrithione, N-(fluorodichlorothio) phthalimide, 2,4,5,6-tetrachloro-1,3-isophthalonitrile, 2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine, N,N-dimethyl-N′-phenyl-N′-(fluorodichlorothio) sulfamide, 3-jodo-2-propynyl butyl carbamate, 4,5-dichloro-2-n-octyl-4-isothiazoline-3-on and the like,

(B) preferable members:

copper hydroxide, triphenyl tin hydroxide, triphenyl tin chloride, zinc powder, N-(trichloromethylthio)-phthalimide, N-(tetrachloroethylthio)-tetraphthalimide, N,N-dimethyl-N′-(fluorodichloromethylthio)-sulfamide, 2-benzimidazole carbamic acid methyl, benzyl isothiocyanate, N-n-octyl-isothiazolone, dimethyl dithiocarbamic bromide and the like.

(C) least preferable members:

bistriphenyl tin oxide, quinoline, triphenyl tin acetate, zinc hydroxide and the like.

At least one of the abovesaid antifouling agents may be advantageously used. Other antifouling agents may be used together, as desired.

Among them copper powder is very useful when combined with other antifouling agent, because of exhibiting a synergistic effect and providing a good storage stability. When an antifouling agent is compounded with heretofore proposed triorgano tin salt of high molecular weight substance (known hydrolysis type resin), there are often reactions between the resin and the antifoulig agent used. However, the present resinous vehicle is inert to these antifouling agents, and therefore, it is possible to get a stable coating composition and a reliable antifouling efficiency of the coating.

(2) Plasticizer and hydrolysis regulator:

As the plasticizer and hydrolysis regulator, any of the known materials having solubility in water of up to 1% by weight may be satisfactorily used.
This is because, if the solubility is over 1% by weight, the used plasticizer and hydrolysis regulator are selectively dissolved out of the coating by seawater and stable plasticizing and hydrolyzing effects can hardly be obtained. Examples of such plasticizers are phthalic acid esters as dibutyl phthalate, dimethyl phthalate, dicyclohexyl phthalate and the like, aromatic dibasic acid esters as bis(butoxy ethyl) adipate, dibutyl sebacate and the like, glycol esters as triethylene glycol dibenzoate, pentaerythritol alkyl ester and the like, epoxidized fatty acid esters as tri(epoxy stearin) butyl, trioctyl epoxystearate and the like, epoxy fatty acid triglycerides as epoxy soybean oil, epoxy octyl stearate and the like, organic phosphoric acid esters as dibutyl phosphate, octyl diphenyl phosphate, tricresyl phosphate and the like, fatty acid esters as butyl oleate, octyl tallate and the like, chlorinated paraffins, camphor, triacetylene and the like.

(3) Hydrolysis regulator:

Examples of such hydrolysis regulators are chlorinated paraffin, polyvinyl ether, dihydroabietyl sebacate, partially hydrogenated terphenyl, polyvinyl acetate, polyalkyl fumarate, polyether polyol, alkyd resin, polyester resin, polyurethane and the like.

(4) Pigment:

For example, body pigments as baryte, precipitated barium sulphate, talc, kaoline, chalk, shell white, alumina white, titanium white, bentonite and the like; color pigments as titanium peroxide, titanium oxide, basic lead sulfate, tin oxide, carbon black, graphite, red iron oxide, chrome green, emerald green, phthalocyanine blue, and the like.

(5) Solvent:

For example, hydrocarbons (e.g. xylene, toluene, benzene, ethyl benzene, cyclopentane, octane, heptane, cyclohexane, white spirit and the like), ethers (e.g. dioxan, tetrahydrofuran, ethyl ether, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and the like), esters (e.g. butyl acetate, propyl acetate, benzyl acetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate and the like), ketones (e.g. methyl isobutyl ketone, ethyl isobutyl ketone and the like), alcohols (e.g. n-butanol, propyl alcohol and the like), and the like.

(6) Other additives:

For example, organic monobasic acids (e.g. rosin, naphthenic, palmitic, linoleic, soybean, tall oil and the like), hardened castor oil and the like.

The present antifouling paint can be prepared by the method known per se in the art by using the predetermined amounts of the above components.

The present inventors have also found that by the incorporation of a specific amount of pyrithione containing compound as described in Japanese Patent Application Laid-Open No. 154778/88 in the present coating composition as exemplified in Examples 16 to 22, it is possible to shorten the kneading time required for the formulation of said paint and improve the dispersion stability of the obtained paint. Since the vehicle resin contains metals, amine, amidation compound, or part thereof as alkali metal salt, alkali earth metal salt, copper, tin and the like, during long term storage before the coating, the pigment in the paint, especially the cuprous oxide pigment and the like, tends to be oxidized by the oxygen dissolved in the paint, thereby causing a change in the color of the paint. However, the addition of the pyrithione containing compound to the paint composition of the present invention can prevent the color change of the paint during storage.

If necessary, various pigments, dyestuffs, plasticizers, stabilizers, thixotropic agents, dehydrating agents, anti-sagging agents, anti-settling agents, surface active agents, and the like may be added to the present antifouling paint composition.

The present antifouling paint composition can be applied to various substrates such as wood, paper, leather, asbestos, glass, plastics, fiber, metal, concrete, and the like, which are used underwater. It is particularly suitable for the coating of the surface of ships, fishing nets, fishing gears, and the like.

Furthermore, since the present antifouling paint can be formulated without the necessity of being fully relied on an expensive and toxic triorgano tin compound, the manufacturing cost can be markedly lowered and hygienic problems can be effectively obviated.

The present paint is totally free from low boiling organic basic acid and therefore, there is no fear of forming blisters in the formed coating. Thus, the present antifouling paint is quite useful for the coating of various substrates as ships, marine structures, fish nets and the like.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and % are by weight.

Preparation of base resin varnishes

Reference Example 1

Into a 4-necked flask fitted with a stirrer, a reflux condenser, a nitrogen gas inlet tube and a dropping funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 110° to 110° C. To this, a mixture of 25.7 parts of acrylic acid, 57.8 parts of ethyl acrylate, 16.5 parts of methyl methacrylate and 3 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the combined mixture was maintained at 110° C for 30 minutes, added dropwise with a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then maintained at the same temperature for 2 hours to obtain a resinous varnish (A) having a solid content of 39.6 wt % and a solid acid value of 200 mg KOH/g. The number average molecular weight (polystyrene conversion) of the resin contained was 11000.

Reference Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 90 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to 110° C. To this, a mixture of 7.7 parts of methacrylic acid, 64.4 parts of methyl methacrylate, 28 parts of 2-ethyl hexyl acrylate and 2 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 110° C for 30 minutes, added dropwise with a mixture of 30 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (B) having a solid content of 39.8 wt % and a solid acid value of 50 mg KOH/g. The number average molecular weight of the resin contained was 15000.

Reference Example 3

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to 110° C. To this, a mixture of 38.5 parts of acrylic acid, 50.9 parts of ethyl acrylate, 10.6 parts of n-butyl acrylate and 3 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 110° C for 30 minutes, dropwise added with a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (C) having a solid content of 39.4 wt % and a solid acid value of 300 mg KOH/g. The number average molecular weight of the resin contained was 12000.

Reference Example 4

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were place 80 parts of xylene and 20 parts of n-butanol and the mixture was heated to 80° to 90° C. To this, a mixture of 38.5 parts of acrylic acid, 45.8 parts of ethyl acrylate, 15.7 parts of methyl methacrylate and 1.5 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 90° C for 30 minutes, dropwise added with a mixture of 40 parts of xylene, 10 parts of n-butanol and 0.5 parts of azobisisobutyronitrile in 1 hour and then heated at the same

temperature for 2 hours to obtain a resinous varnish (A) having a solid content of 60.8 wt% and a solid acid value of 300 mg KOH/g. The number of average molecular weight of the resin contained was 3700.

Example 1

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 25.0 parts of zinc acetate, 40.3 parts of oleic acid and 120 parts of xylene and the mixture was heated to 120°C and maintained at the same temperature, while removing the formed acetic acid with said solvent. The end point of said reaction was settled by determining the quantities of acetic acid in the distillate and the reaction was stopped after elapsing 12 hours. Thus obtained varnish-1 had a solid content of 55.8 wt% and a viscosity of B-S.

Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter were placed 100 parts of the resinous varnish (C) obtained in Reference Example 3, 44 parts of copper propionate, 60 parts of naphthenic acid, 0.1 part of butane sulfonic acid and 20 parts of deionized water and the mixture was heated to 100°C and maintained at the same temperature, while removing the formed propionic acid azeotropically with water. The end point of said reaction was determined by checking the amount of propionic acid in the distillate. The remaining amounts of water were completely removed, the reaction was stopped after 7 hours' reaction and xylene was then added to the reaction mixture. Thus obtained varnish-2 had a solid content of 52.3 wt% and a viscosity of P.

Example 3

Into a 3-necked flask fitted with a reflux condenser, a stirrer and a decanter, were placed the resinous varnish (B) obtained in Reference Example 2, 8.1 parts of manganese acetate and 7.8 parts of 2,4-dimethylphenoxy acetate and the mixture was heated to 70°C and maintained at the same temperature for 10 hours. The formed acetic acid was continuously removed under reduced pressure and after completion of the reaction, 35 parts of xylene were added to obtain varnish-3 having a solid content of 50.3 wt% and a viscosity of D.

Example 4

Into a similar reaction vessel as used in Example 1, were placed 100 parts of the resinous varnish (C) obtained in Reference Example 4, 37.0 parts of cobalt acetate, 12.1 parts of linseed oil and 120 parts of xylene and the mixture was heated and reacted while removing the formed acetic acid with the solvent for 12 hours. Thus obtained varnish-4 had a solid content of 56.2 wt% and a viscosity of I.

Example 5

The similar experiment as stated in Example 4 was repeated excepting substituting 65.1 parts of germanium acetate for 37.0 parts of cobalt acetate and 196 parts of versatic acid for 82.1 parts of versatic acid. Thus obtained varnish-5 had a solid content of 54.8 wt% and a viscosity of Z-2.

Example 6

[illegible]

varnish-6 had a solid content of 52.8 wt% and a viscosity of P.

Example 7

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 42.5 parts of zinc dilactate trihydrate, 28.6 parts of SA-13 (trademark of Idemitsu Sekiyu, branched type monocarboxylic acid, average carbon number 13) and 100 parts of xylene and the mixture was heated to 120°C and reacted at the same temperature while removing the formed lactic acid with xylene. Thus obtained varnish-7 had a solid content of 54.2 wt% and a viscosity of Q.

Example 8

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 37 parts of nickel valerate, 22.6 parts of SA-9 (trademark of Idemitsu Sekiyu, branched type monocarboxylic acid, average carbon atoms 9), and 95 parts of xylene and the mixture was heated to 140°C and reacted at the same temperature while removing the formed valeric acid with xylene. Thus obtained varnish-8 had a solid content of 55.1 wt% and a viscosity of O.

Example 9

The same procedures as stated in Example 3 were repeated excepting substituting a mixture of 100 parts of the resinous varnish (C) obtained in Reference Example 3, 99.1 parts of lead enanthate and 62 parts of versatic acid for the materials shown in Example 3 and changing the reaction temperature to 140°C. Thus obtained varnish-9 had a solid content of 52.7 wt% and a viscosity of R.

Example 10

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (B) obtained in Reference Example 2, 9.9 parts of magnesium cyclohexane carboxylate, 4.4 parts of nicotinic acid and 20 parts of deionized wtaer and the mixture was reacted as in Example 2. Thus obtained varnish-10 had a solid content of 53.4 wt% and a viscosity of R.

Example 11

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were place 100 parts of the resinous varnish (A) obtained in Reference Example 1, 39.9 parts of aluminium cyclopropane carboxylate, 72.4 parts of 2,4-dichlorophenoxy acetate and 125 parts of xylene and the mixture was heated to 140°C and reacted as in Example 1, to obtain varnish-11 having a solid content of 51.8 wt% and a viscosity of V.

Example 12

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 34.7 parts of tellurium acetate, 40 parts of naphthenic acid, 0.2 part of butylene sulfonic acid and 110 parts of xylene and the mixture was reacted as in example 1 for 8 hours to obtain varnish-12 having a solid content of 52.4 wt% and a viscosity of S.

Example 13

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a thermometer were placed 100 parts of the resinous varnish B obtained in Reference Example 2, 10.4 parts of cobalt acetate, 7.1 parts of SA-13 and 115 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-13 having a solid content of 53.4 wt% and a viscosity of V.

Example 14

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a thermometer were placed 100 parts of the resinous varnish A) obtained in Reference Example 1, 32.4 parts of chromium acetate, 30.7 parts of oleic acid and 130 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-14 having a solid content of 51.8 wt% and a viscosity of U.

Example 15

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a thermometer were placed 100 parts of the resinous varnish D) obtained in Reference Example 4, 62.1 parts of cobalt acetate, 62.1 parts of versatic acid and 150 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-15 having a solid content of 54.7 wt% and a viscosity of X.

Example 16

Using a resinous varnish B) obtained in Reference Example 2, 10 parts of titanium acetate, 18.0 parts of penicillic acid and 50 parts of xylene and the reaction temperature of 75° to 80°C, the similar experiment as stated in Example 3 was repeated to obtain varnish-16 having a solid content of 52.8 wt% and a viscosity of Y.

Example 17

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a thermometer were placed 100 parts of the resinous varnish C) obtained in Reference Example 3, 59.0 parts of titanium acetate, 101 parts of 2,4-dichlorophenoxyacetate and 160 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-17 having a solid content of 56.2 wt% and a viscosity of Z.

Example 18

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a thermometer were placed 100 parts of the resinous varnish C) obtained in Reference Example 3, 40 parts of cobalt acetate, 60 parts of naphthenic acid and 110 parts of xylene and the mixture was heated at 120°C while removing the formed acetic acid out of the system. Thus obtained varnish-18 had a solid content of 53.6 wt% and a viscosity of W.

Comparative Example 1

The reaction was carried out in the same manner as in Example 3 except that the titanium acetate was not

Comparative Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a thermometer

110°C for 30 minutes, a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile was dropwise added in 1 hour and the combined mixture was heated at the same temperature for 2 hours to obtain Comparative varnish 3 having a solid content of 39.6 wt%.

Comparative Example 3

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 10.3 parts of zinc hydroxide, 60 parts of oleic acid and 110 parts of xylene and the mixture was heated at 100 to 120°C while removing water with the solvent. Thus obtaine varnish (Comparative varnish-3) had a solid content of 55.8% and a viscosity of Z_2.

Comparative Example 4

Into a 3-necked flask fitted with a reflux condenser, a stirrer and a nitrogen gas inlet tube, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1 and 68 parts of zinc oleate, and the mixture was reacted at 120°C for 3 hours. Thus obtained varnish (Comparative varnish-4) had a solid content of 62% and a viscosity of M to N.

Comparative Example 5

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 13 parts of zinc hydroxide and 105 parts of kylene and the mixture was heated at 120°C. During the reaction, certain amounts of water were distilled off, but after elapsing 30 minutes from the commencement of said reaction, the content was turned to gel and no uniform resinous solution was obtained.

Comparative Example 6

Into a similar reaction vessel as used in Comparative Example 1, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 16.6 parts of copper hydroxide, 60 parts of naphthenic acid and 110 parts of xylene and the mixture was heated at 120°C while removing water with the solvent. After elapsing 2 hours from the commencement of the reaction, the content was turned to gel and no uniform resinous solution was obtained.

Example 19

45 parts of varnish-1 obtained in Example 1, 30 parts of cuprous oxide, 5 parts of zinc bis (dimethyl dithiocarbamate), 3 parts of colloidal silica, 5 parts of xylene, 10 parts of methyl isobutyl ketone and 2 parts of n-butonal were placed in a ball mill and the mixture was subjected to a dispersion operation for 5 hours to obtain a coating composition containing particles with maximum diameter of 35μ.

Example 20 to 58 and Comparative Examples 5 to 9

Using the materials shown in Table 1 and following the method stated in Example 19, the respective coating compsoition was prepared.

Table 1

Example	20	21	22	23	24	25	26
varnish 1	35	30					
varnish 2			40	45			
varnish 3					25		
varnish 4						40	
varnish 5							35
varnish 6							
varnish 7							
varnish 8							
varnish 9							
varnish 10							
Note 1	20			15		15	
Note 2		20			15		
Note 3			25				
Note 4							
Note 5						3	
Note 6		10					15
Note 7				5			
Note 8	10						
Note 9					10		
Note 10						5	
Note 11						10	
Note 12					5		5
Note 13							
Note 14			5				
Note 15							10
Note 16		5			10		
Note 17							
Note 18			5				5
Note 19		5		5			
Note 20				5	5		
Note 21			5				
Note 22					5		
Note 23	5	5	5	2			
Note 24	10		5	5		5	10
Note 25	5	5	5	3		5	
Note 26	3	3	3	3	3	3	3
Note 27		10					
Note 28	10	5		5	20	10	10
Note 29	2	2	2	2	2	4	2
total	100	100	100	100	100	100	100

Table 1 (continued)

Example	27	28	29	30	31	32
varnish 1						
varnish 2						
varnish 3						
varnish 4						
varnish 5						
varnish 6	30					
varnish 7		35				
varnish 8			30			
varnish 9				35		
varnish 10					40	45
Note 1	25		30		20	
Note 2				30		
Note 3		20				
Note 4	5					
Note 5				5		
Note 6						10
Note 7			10		5	
Note 8					5	
Note 9						
Note 10						
Note 11						
Note 12				10		15
Note 13		10				
Note 14	5					
Note 15						
Note 16				5		
Note 17		10	5			
Note 18	5					10
Note 19	5	5				
Note 20	5		5			
Note 21		5				
Note 22				5		
Note 23	5	5				
Note 24			5		5	
Note 25	5					
Note 26	3	3	3	3	3	3
Note 27	5		5	5	10	5
Note 28		5	5		10	10
Note 29	2	2	2	2	2	2
total	100	100	100	100	100	100

Table 1 (continued)

Example	33	34	35	36	37	38	39	40	41	42
varnish 1	35	40								
varnish 2			35	40						
varnish 3					35	40				
varnish 9							40			
varnish 10								35		
varnish 11									40	
varnish 12										35
varnish 13										
varnish 14										
varnish 15										
varnish 16										
varnish 17										
varnish 18			10							
Note 1'	25				10	15		5		
Note 2'				25						15
Note 3'		30			15		10	10		
Note 4'			25				15		15	
Note 5'			10							
Note 6'		15					5			
Note 7'								10		
Note 8'					10				10	
Note 9'	10			10		5				
Note 10'										5
Note 11'										
Note 12'						5				
Note 13'										
Note 14'										5
Note 15'										
Note 16'					5					
Note 17'			5							
Note 18'							10			
Note 19'		5							5	
Note 20'			5	5	10	10			10	10
Note 21'	5					5		10		5
Note 22'			5	5	5			10	5	5
Note 23'	10	5		10		5	5	5	5	10
Note 24'	3	3	3	3	3	3	3	3	3	3
Note 25'	10				5	10	10	10	5	5
Note 26'	2	2	2	2	2	2	2	2	2	2
total	100	100	100	100	100	100	100	100	100	100

Table 1 (continued)

Example	43	44	45	46	47	48	49	50	51
varnish 1									
varnish 2								10	5
varnish 3									
varnish 9									
varnish 10									
varnish 11									
varnish 12									
varnish 13	35								
varnish 14		40							
varnish 15			40						
varnish 16				45					
varnish 17					40				
varnish 18						45	40	30	35
Note 1'	15		15				25	20	
Note 2'		5			15	20			25
Note 3'		10						5	
Note 4'									
Note 5'									
Note 6'									
Note 7'				15					
Note 8'					10				
Note 9'							5		
Note 10'									
Note 11'	10					10	10		
Note 12'			10						5
Note 13'								10	
Note 14'									10
Note 15'	5		5						
Note 16'					10				
Note 17'		10		15					
Note 18'									
Note 19'		5							
Note 20'	10	10	10	15	10	10	10		10
Note 21'		5						15	
Note 22'	5		5		5	5		5	
Note 23'			5		5	5			5
Note 24'	3	3	3		3	3	3	3	3
Note 25'	15	10	5	10			5		
Note 26'	2	2	2		2	2	2	2	2
total	100	100	100	100	100	100	100	100	100

Table 1 (continued)

Example	52	53	54	55	56	57	58
varnish 1	35	35					
varnish 2			45	40			
varnish 3					35	35	
varnish 4							40
varnish 15							
varnish 16							
varnish 17							
varnish 18							
Note 1"	5					10	
Note 2"		10					
Note 3"			5	10			
Note 4"		5					10
Note 5"	10		10			5	
Note 6"		5					
Note 7"		10	15			15	
Note 8"	15				15		25
Note 9"		5					
Note 10"	5						
Note 11"				5			
Note 12"						10	
Note 13"				5			
Note 14"					10		
Note 15"			5				
Note 16"	5						
Note 17"		5					
Note 18"					10		10
Note 19"					5		
Note 20"	5						
Note 21"	5	10	5	5		5	10
Note 22"	5	5	5	10	5	5	
Note 23"	3	3	3	3	3	3	3
Note 24"		10	5	10	15	10	
Note 25"	5			10			
Note 26"	2	2	2	2	2	2	2
total	100	100	100	100	100	100	100

Table 1 (continued)

Comparative Example	7	8	9	10	11
Comparative varnish 1	45				
Comparative varnish 2		45			
Comparative varnish 3			23		
Comparative varnish 4				45	
varnish 1					35
cuprous oxide	30	30	15	30	
Zn bis (dimethyl dithiocarbamate)	5	5	2	5	
copper sulfate					25
dioctyl phthalate					5
titanium oxide					5
talc					5
xylene	5	5	46	5	10
colloidal silica	3	3	2	3	3
red iron oxide					5
methyl isobutyl ketone	10	10	10	10	5
n-butanol	2	2	2	2	2
total	100	100	100	100	100

In Comparative Example 7, paint viscosity was very high, and therefore, a larger quantity of xylene was used.

Note 1 : cuprous oxide

Note 2 : zinc white

Note 3: copper rhodanide

Note 4: Cu powder

Note 5: Zn powder

Note 6: copper hydroxide

Note 7: 2-thiocyanomethylthio benzothiazole

Note 8: N-(fluorodichloromethylthio) phthalimide

Note 9: N-(trichloromethylthio) phthalimide

Note 10: N-(tetrachloroethylthio) tetraphthalimide

Note 11: benzyl isothiocyanate

Note 12: quinoline

Note 13: 8-hydroquinoline

Note 14: zinc pyrithione

Note 15: triphenyl tin acetate

Note 16: bis-triphenyl tin oxide

Note 17: 3-Jod-2-propynyl butyl carbamate

Note 18: tricresyl phosphate

Note 19: polyvinyl ether

Note 20: chlorinated paraffin wax

Note 21: polyether polyol

Note 22: dioctyl phthalate

Note 23: talc

Note 24: titanium oxide

Note 25: red iron oxide

Note 26: colloidal silica

Note 27: methyl isobutyl ketone

Note 28: xylene

Note 29: n-butanol

Note 1': cuprous oxide

Note 2': copper rhodanide

Note 3': zinc white

Note 4': copper hydroxide

Note 5': N,N-dimethyl-N'-(fluorodichloromethylthio) sulfamide

Note 6': 2-benzimidazole carbamic methyl

Note 7': benzyl isothiocyanate

Note 8': N-n-octyl-isothiazolone

Note 9': N N-dimethyl-N'-phenyl-N'-(fluorodicyclomethylthio) sulfamide

Note 10': Zn bis (dimethyl dithiocarbamate)

Note 11': Zn ethylene bis (dithiocarbamate)

Note 12': Mn ethylene bis (dithiocarbamate)

Note 13': Cu bis (dimethyl dithiocarbamate)

Note 14': 2,4,5,6-tetrachloro-1,3-isophthalonitrile

Note 15': 2,3,5,6-tetrachloro-4-(methyl sulfonyl) pyridine

Note 16': 4,5-dichloro-2-n-octyl-4-isothiazoline-3-on

Note 17': dimethyl dithiocarbamic acid bromide

Note 18': triphenyl tin hydroxide

Note 19': triphenyl tin chloride

Note 20': chlorinated paraffin wax

Note 21': dioctyl phthalate

Note 22': titanium oxide

Note 23': red iron oxide

Note 24': colloidal silica

Note 25': xylene

Note 26': n-butanol

Note 1": chlorinated polyethylene

Note 2": chlorinated polypropylene

Note 3": triamyl citrate

Note 4": isobutyl tartarate

Note 5": polyether polyol

Note 6": copper naphthenate

Note 7": cuprous oxide

Note 8": zinc white

Note 9": 2,4-(thiazolyl) benzoimidazole

Note 10": 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole

Note 11": phenothiazole

Note 12": α-nitrostyrene sulfathiazole

Note 13": nitro acridine

Note 14": sulfathiazole

Note 15": tetraphenyl boron pyridinium

Note 16": thiabendazole

Note 17": N-(1,1,2,2-tetrachloroethylthio)-cyclohexene-1,2-dicarboxyimide

Note 18": α-chloro-α-phenyl acetyl urea

Note 19": 2-methyl carboxy-amino-benzimidazole

Note 20": talc

Note 21": titanium oxide

Note 22": red iron oxide

Note 23": colloidal silica

Note 24": xylene

Note 25": methyl isobutyl ketone

Note 26": n-butanol

The coating compositions obtained in Examples 19 to 58 and Comparative Examples 5 to 9 each was applied onto a test plate in about 200μ dry thickness, and thus prepared test plate was attached to Discrotor, immersed in sea water (16° to 23° C) and rotated at a constant speed (peripheral speed about 30 knots) for 3 months (days and nights). Use-up rate of the coating was determined microscopically. The results are show in Table 2.

Table 2

Example	Initial film thickness (Å)	Coating removed after 3 hours (Å)	Coating removed after 6 hours (Å)
9	190	160	30
20	210	185	25
21	190	155	35
22	190	155	35
23	200	160	40
24	200	185	15
25	185	160	25
26	210	180	30
27	175	150	25
28	190	160	30
29	180	150	30
30	190	155	35
31	180	170	10
32	190	175	15
33	190	160	30
34	185	150	35
35	200	160	40
36	200	165	35
37	210	190	20
38	185	170	15
39	190	150	40
40	205	195	10
41	195	180	15
42	185	165	20
43	205	190	15
44	210	185	25
45	191	169	22
46	210	195	15
47	195	174	21
48	210	180	30
49	205	180	25
50	200	170	30
51	195	160	35
52	195	160	35
53	200	170	30
54	190	155	35
55	191	150	41
56	208	190	18
57	201	181	20
58	191	156	35
Comparative Example			
1	200	0	200
2	190	180	10
3	174	138	36
4	191	135	56
5	195	35	160

Table 3

Antifouling test

(surface area % adhered with submarine living)

Example	19	20	21	22	23	24	25	26	27	28	29	30	31
Duration (months)													
2	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0
26	0	5	0	0	0	5	0	0	0	0	0	5	0
28	0	15	0	0	5	10	0	5	0	0	0	15	0
30	3	20	0	5	10	15	10	15	0	0	0	20	0

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Example	32	33	34	35	36	37	38	39	40	41	42	43	44
Duration (months)													
2	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0
26	5	0	0	0	0	0	0	0	0	0	0	0	0
28	15	0	5	0	0	0	0	3	0	0	0	0	0
30	20	0	15	10	0	3	0	10	10	5	0	0	3

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Example	45	46	47	48	49	50	51	52	53	54	55	56	57	58
Duration (months)														
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	*	*	*	*	*	*	*
28	0	0	0	0	0	0	0	*	*	*	*	*	*	*
30	0	10	3	5	0	0	0	*	*	*	*	*	*	*

* ... unexamined

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Comparative Example	7	8	9	10	11
Duration (months)					
2	0	0	0	0	0
4	0	30	0	0	0
6	100	80	0	0	0
6	100	100	0	0	0
10	100	100	0	0	0
12	stopped	100	10	5	0
14		stopped	30	20	0
16			100	70	30
18			100	100	100
20			100	100	100

Visual examination of surface conditions:

After conducting the aforesaid immersion test, the coated plate was examined by naked eyes on the surface conditions. No blisters and cracks were found on the coated plates of Examples 19 to 58. In Comparative Example 7, cracks were observed after 12 months' immersion test and in Comparative Example 8, blisters were observed after 10 months' immersion test.

The present invention thus provides a novel process for the preparation of metal containing, hydrolysis type resin composition which is very useful as resinous vehicle for an antifouling paint having excellent storage stability and weatherability dissolution properties. This process is also suitable for the preparation of such resin compositions with a variety of metal species in comparatively higher yields. The present resin composition can be freely compounded with a variety of antifouling agents and thus obtained antifouling paints are characterized in resulting coatings which are free from cracks and ion exchange and have excellent long-lasting antifouling effects.

Claims

1. A process for preparing metal-containing resin composition comprising the steps of:

A) providing a metal containing resin having

B) metal [illegible]

C) [illegible]

2. A process according to claim 1, wherein the metal is selected from the members belonging to Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, VIa, VIb, VIIa and VIII groups of Periodic Table.

3. A process according to claim 2, wherein the metal is selected from zinc, copper and tellurium.

4. A process according to claim 1, wherein the low boiling organic basic acid has a boiling point of 100 to 240° C and the high boiling organic monobasic acid has a boiling point which is at least 20° C higher than the boiling point of said low boiling organic basic acid.

5. A process according to claim 1, wherein the high boiling organic monobasic acid has an antifouling property.

6. A process according to claim 1, wherein the reaction is carried out in the presence of water, while removing the formed low boiling organic basic acid azeotropically with said water.

7.A process according to claim 1, wherein the low boiling organic basic acid is removed under reduced pressure.

8.A process according to claim 1, wherein the reaction is carried out in the presence of an organic solvent and the formed low boiling organic basic acid is removed out of the system azeotropically with said organic solvent.

9. An antifouling paint containing as resinous vehicle a metal containing resin composition prepared by the method wherein a mixture of

(A) acid group containing base resin.

(B) metallic salt of low boiling organic basic acid, in which the metal is selected from the members having 2 or more valence and lesser ionization tendency than those of alkali metals, and

(C) high boiling organic monobasic acid

is reacted at an elevated temperature while removing the formed low boiling organic basic acid out of the system.

10. An antifouling paint according to claim 9, wherein the metal is selected from the members belonging to Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, VIa, VIb, VIIa and VIII groups of Periodic Table.

11. An antifouling paint according to claim 10, wherein the metal is selected from zinc, copper and tellurium.

12. An antifouling paint according to claim 9, wherein the acid group containing base resin has an acid value of 25 to 350 mg KOH/g.

13. An antifouling paint according to claim 9, wherein the low boiling organic basic acid has a boiling point of 100 to 240° C and the high boiling organic monobasic acid has a boiling point which is at least 20° C higher than the boiling point of said low boiling organic basic acid.

14. An antifouling paint according to claim 9, wherein the high boiling organic monobasic acid has an antifouling property.

15. An antifouling paint according to claim 9, which further contains either one or combination of two or more of organic antifouling agent, inorganic antifouling agent, plasticizer, hydrolysis regulator, pigment, solvent and other conventional additives.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 0970

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A-2 058 801 (RHONE-POULENC) * Claims 1-18; page 3, lines 48-52 * ---	1	C 08 F 8/44 C 09 D 5/14
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 365 (C-460)[2812], 27th November 1987; & JP-A-62 135 575 (KANSAI PAINT CO. LTD) 18-06-1987 -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 F
C 09 D

The present search report has been drawn up for all claims

Date of search	Date of completion of the search	Examiner
THE HAGUE	24-01-1989	PESMENTIER M.A.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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